

# A model of solid-solution interactions in acid organic soils, based on the complexation properties of humic substances

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## SUMMARY

CHAOS (Complexation by Humic Acids in Organic Soils) is a quantitative chemical model of organic soils that incorporates complexation by the functional groups of humic substances and non-specific ion-exchange reactions. The two types of interaction are linked by the net humic charge,  $Z$ , which depends on the extents of proton and metal complexation, and which in turn determines ionic concentrations in the diffuse part of the electrical double layer, by a Donnan equilibrium. CHAOS was found to account satisfactorily for the results of acid–base titration experiments (pH range 3–5) with soil samples, giving reasonable simultaneous predictions of solution pH and concentration of  $Al^{3+}$ . Predictive calculations with CHAOS suggest that organic soils acidified by acid rain would respond on a time-scale of years-to-decades to reductions in rain acidity. An associated effect might be an increase in the concentration of dissolved organic matter in the soil solution.

## INTRODUCTION

In the upper horizons of acid soils, solution composition is determined primarily by interactions between dissolved species and solid organic matter (Krug & Frink, 1983; Bache, 1984). The interactions involve  $H^+$ ,  $Al^{3+}$ ,  $AlOH^{2+}$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$  and  $K^+$  in solution, and humic  $COOH$  and weaker acid groups, together with non-specific cation-exchange sites, in the solid phase. Their quantitative description would be useful in understanding (a) the effects of acid deposition, (b) podzolization, and (c) how the organic content of drainage waters is determined. The last is important to the Water Industry because of the need to remove ‘dissolved colour’ before water is acceptable for domestic supply.

In this paper we present a quantitative model of acid organic soils, based on the complexation properties of humic substances (HS), the dominant soil ingredients with respect to interactions with the aqueous phase. The soil is treated as a concentrated suspension of HS. Complexation reactions are described by combinations of intrinsic equilibrium constants and electrostatic terms, non-specific cation-exchange by a Donnan equilibrium. The two types of reaction are linked via  $Z$ , the net humic charge. The model is based on a previous one for HS in natural waters (Tipping *et al.*, 1988a) and is referred to as CHAOS (Complexation by Humic Acids in Organic Soils). Firstly, the formulation of CHAOS is described, next its ability to account for the results of experiments with soil suspensions is considered, and lastly its use for predictive modelling is explored.

## MODEL FORMULATION

A schematic diagram of the reactions involved in CHAOS is given in Fig. 1. Cationic species (restricted to  $H^+$ ,  $Al^{3+}$ ,  $AlOH^{2+}$ ,  $Ca^{2+}$  and  $Na^+$  for ease of presentation) occur in three compartments,  $H$ ,  $D$  and  $S$ . Compartment  $H$  is the humic material itself, able to form complexes with the

	H	D	S
(I)-COOH			
(II)-COOH			
(I)-COO <sup>-</sup>		H <sup>+</sup>	H <sup>+</sup>
(II)-COO <sup>-</sup>			
WAH			
(I)-COO } Al <sup>3+</sup> , AlOH		Al <sup>3+</sup>	Al <sup>3+</sup>
(II)-COO } Al <sup>3+</sup> , AlOH		AlOH <sup>2+</sup>	AlOH <sup>2+</sup>
(I)-COO } Al <sup>3+</sup> , AlOH		Al(OH) <sub>2</sub> <sup>+</sup>	Al(OH) <sub>2</sub> <sup>+</sup>
WA } Al <sup>3+</sup> , AlOH			
(II)-COO } Al <sup>3+</sup> , AlOH			
WA } Al <sup>3+</sup> , AlOH			
(I)-COO } Ca		Ca <sup>2+</sup>	Ca <sup>2+</sup>
(II)-COO } Ca			
(I)-COO } Ca		Na <sup>+</sup>	Na <sup>+</sup>
WA } Ca			
(II)-COO } Ca			X <sup>-</sup>
WA } Ca			

Fig. 1. Species considered in CHAOS.

cations. In compartment *D*, the diffuse part of the electrical double layer, cations are held purely by electrostatic attraction to the (net) negatively charged HS. Compartment *S* is the bulk solution. Two charge balances are required to describe this situation: the net charge of compartments *H* and *D* is zero, as is that of compartment *S*, where cationic charge is balanced by non-interacting (strong acid) anions, designated by X<sup>-</sup>. In the model the concentration of HS is expressed in terms of the volumes of the aqueous compartments *D* and *S*, so that a concentration of  $x \text{ g HS l}^{-1}$  means that for every  $x \text{ g}$  of HS, compartments *D* and *S* together occupy a volume of 1 l. For each litre of (*D* + *S*) there are  $V_D$  litres of *D* and  $V_S$  litres of *S*, so that  $V_D + V_S = 1$ .

Complexation by HS is accounted for in CHAOS as in model III of Tipping *et al.* (1988a). That paper should be consulted for details; the following is a brief account. Contents of humic complexing groups are chosen on the basis of published information (Thurman, 1985), simplification being introduced to make it possible to incorporate competitive interactions reasonably easily. The HS are assumed to have two types of carboxyl group, I and II, both of which undergo dissociation at  $\text{pH} \leq 7$ . In addition there are weaker acid groups (WAH) that dissociate only at higher pH values, but which can exchange a proton for a metal ion at  $\text{pH} \leq 7$ . These WAH groups would include, for example, weak COOH groups and phenolic OH groups. The metal ions Al<sup>3+</sup>, AlOH<sup>2+</sup> and Ca<sup>2+</sup> bind at bidentate sites of three types: type A consists of a type I COOH and a type II COOH, type BI of a type I COOH and a WAH, type BII of a type II COOH and a WAH. Previous work (Tipping *et al.*, 1988a) has shown that this suite of complexed species is the simplest formulation that can account for the competitive interactions involved. For example, if only one type of COOH group is assumed it is not generally possible to fit proton binding data obtained in the absence of Al or Ca.

The HS are characterized by a total acidity,  $A_c$  (eq g<sup>-1</sup>), which is the sum of the COOH and WAH groups. Estimation of total humic acidity is not straightforward (Perdue, 1985), and even if an

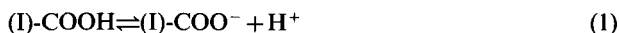
accurate value can be obtained there is no guarantee that all the ionizable groups will be able to participate in metal and proton binding at environmentally-relevant pH values. In our studies (Tipping *et al.*, 1988a) we estimated  $Ac$  by titration to the arbitrarily chosen pH of 11.5, and the values obtained are best regarded as first approximations to the true (effective) values. In data-fitting the model it is found that the estimate of the content of carboxyl groups ( $n$ , eq g<sup>-1</sup>) has a small

**Table 1.** Intrinsic and charge-dependent equilibrium constants

$K_I$	$= \frac{[(I)-COO^-] \{H^+\}}{[(I)-COOH]}$	$K_I(Z)$	$= K_I e^{2wZ}$
$K_{II}$	$= \frac{[(II)-COO^-] \{H^+\}}{[(II)-COOH]}$	$K_{II}(Z)$	$= K_{II} e^{2wZ}$
$K_{A,Al}$	$= \frac{\left[ \begin{array}{c} (I)-COO \\ (II)-COO \end{array} \right] Al^+ \{H^+\}^2}{[(I)-COOH] [(II)-COOH] \{Al^{3+}\}}$	$K_{A,Al}(Z)$	$= K_{A,Al} e^{-2wZ}$
$K_{BI,Al}$	$= \frac{\left[ \begin{array}{c} (I)-COO \\ WA \end{array} \right] Al^+ \{H^+\}^2}{[(I)-COOH] [WAH] \{Al^{3+}\}}$	$K_{BI,Al}(Z)$	$= K_{BI,Al} e^{-2wZ}$
$K_{BII,Al}$	$= \frac{\left[ \begin{array}{c} (II)-COO \\ WA \end{array} \right] Al^+ \{H^+\}^2}{[(II)-COOH] [WAH] \{Al^{3+}\}}$	$K_{BII,Al}(Z)$	$= K_{BII,Al} e^{-2wZ}$
$K_{Al,H}$	$= \frac{\left[ \begin{array}{c} & & \\ & & AlOH \\ & & \end{array} \right] \{H^+\}}{\left[ \begin{array}{c} & & \\ & & Al^+ \\ & & \end{array} \right]}$	$K_{Al,H}(Z)$	$= K_{Al,H} e^{2wZ}$
$K_{A,Ca}$	$= \frac{\left[ \begin{array}{c} (I)-COO \\ (II)-COO \end{array} \right] Ca \{H^+\}^2}{[(I)-COOH] [(II)-COOH] \{Ca^{2+}\}}$	$K_{A,Ca}(Z)$	$= K_{A,Ca}$
$K_{BI,Ca}$	$= \frac{\left[ \begin{array}{c} (I)-COO \\ WA \end{array} \right] Ca \{H^+\}^2}{[(I)-COOH] [WAH] \{Ca^{2+}\}}$	$K_{BI,Ca}(Z)$	$= K_{BI,Ca}$
$K_{BII,Ca}$	$= \frac{\left[ \begin{array}{c} (II)-COO \\ WA \end{array} \right] Ca \{H^+\}^2}{[(II)-COOH] [WAH] \{Ca^{2+}\}}$	$K_{BII,Ca}(Z)$	$= K_{BII,Ca}$

error associated with it, so that uncertainty in  $Ac$  translates to uncertainty in the content of weak acid groups. Since these are modelled in a very rudimentary way, i.e. by assuming them all to be the same, it is probable that uncertainty in their abundance is a minor problem at this stage of model development. The parameter  $Ac$  is also used as an adjustable parameter for 'rescaling' the model to fit field results for natural waters (Tipping *et al.*, 1988b), or, as in this work, to fit laboratory results for soil samples (see below). The content of COOH groups ( $n$ ) consists of  $n/2$  type I groups and  $n/2$  type II groups. It follows that of the total content of bidentate (metal-binding) sites,  $Ac/2$ , there are  $n - (Ac/2)$  type A groups,  $(Ac - n)/2$  type BI groups, and  $(Ac - n)/2$  type BII groups, per g HS.

Relationships between complexed ions and ions in the bulk solution (compartment  $S$ ) are given by expressions that combine an intrinsic equilibrium constant with terms accounting for the electrostatic attraction or repulsion between the humic binding site and the ion in solution. The latter have the general form  $\exp(-2wz_iZ)$  where  $w$  is the 'electrostatic interaction factor',  $z_i$  is the charge of the ion in question, and  $Z$  is the net humic charge (cf. Tanford, 1961). Consider for example the reaction



The equilibrium constant for the (hypothetical) case where there is no electrostatic influence—the intrinsic equilibrium constant—is given by

$$K_1 = \frac{[(I)\text{-COO}^-] \{ \text{H}^+ \}}{[(I)\text{-COOH}]} \quad (2)$$

where square and curled brackets indicate concentration and activity, respectively. The (charge-dependent) equilibrium constant for the case where the HS have a net charge of  $Z$  eq g<sup>-1</sup> is given by

$$K_1(Z) = \frac{[(I)\text{-COO}^-] \{ \text{H}^+ \}}{[(I)\text{-COOH}] \exp(-2wZ)} = K_1 \exp(2wZ) \quad (3)$$

Since  $w$  is positive and  $Z$  invariably negative, the charge-dependent constant is less than the intrinsic one, in this case. In other words, the COOH group is less dissociated, reflecting the attraction of the negatively-charged humic molecule for  $\text{H}^+$ . Table 1 gives expressions for all the complexation reactions that occur in CHAOS. The nine equilibrium constants shown are condensed to five by making the simplifying assumption that

$$K_{A,Al} = K_{BI,Al} = K_{BII,Al} = K_{Al} \quad (4)$$

$$K_{A,Ca} = K_{BI,Ca} = K_{BII,Ca} = K_{Ca} \quad (5)$$

It should be noted that the reactions to which these equilibrium constants refer are formulated as proton-metal exchanges (Table 1), not as ionized ligand-metal associations. Some justification for the assumption of a single constant comes from literature data for simple diprotic acids that correspond to the assumed humic bidentate sites. Thus from Martell & Smith (1977) the following equilibrium constants (at 25°C, zero ionic strength) for the exchange reaction  $\text{LH}_2 + \text{Al}^{3+} \rightleftharpoons \text{LAl}^+ + 2\text{H}^+$  (where  $\text{L}^{2-}$  is the unprotonated ligand) can be calculated; phthalic acid  $10^{-4.0}$ , meso-tartaric acid  $10^{-1.3}$ , salicylic acid  $10^{-2.9}$ , sulphosalicylic acid  $10^{-1.4}$ . Equilibrium constants for the association reaction  $\text{L}^{2-} + \text{Al}^{3+} \rightleftharpoons \text{LAl}^+$  vary much more widely, having values of  $10^{4.3}$ ,  $10^{6.7}$ ,  $10^{14.0}$  and  $10^{13.4}$ , respectively. Values of  $K_{Al}$  for four humic samples were in the range  $10^{-3.3} - 10^{-3.8}$  (Tipping *et al.*, 1988a), similar to those for the simple diprotic acids.

The electrostatic interaction factor,  $w$ , is given by the empirical equation

$$w = P \log_{10}(I) \exp(Q|Z|) \quad (6)$$

where  $P$  and  $Q$  are constants,  $I$  is the ionic strength and  $|Z|$  is the modulus of  $Z$ . It is Equation (6) that takes the effect of ionic strength on humic complexation reactions into account.

Relationships between ionic concentrations in compartments  $D$  and  $S$  are accounted for in the simplest possible way by assuming a Donnan equilibrium (Arnold, 1978). Thus for two cations  $\text{Y}_1^{m+}$  and  $\text{Y}_2^{n+}$  we have

$$(\{ \text{Y}_1^{m+} \}_D / \{ \text{Y}_1^{m+} \}_S)^{1/m} = (\{ \text{Y}_2^{n+} \}_D / \{ \text{Y}_2^{n+} \}_S)^{1/n} \quad (7)$$

It is further assumed that activity coefficients in the two compartments are the same, so that

$$\begin{aligned}
 ([\text{Na}^+]_D/[\text{Na}^+]_S) &= ([\text{H}^+]_D/[\text{H}^+]_S) \\
 &= ([\text{Ca}^{2+}]_D/[\text{Ca}^{2+}]_S)^{\frac{1}{2}} \\
 &= ([\text{Al}^{3+}]_D/[\text{Al}^{3+}]_S)^{\frac{1}{3}} \\
 &= ([\text{AlOH}^{2+}]_D/[\text{AlOH}^{2+}]_S)^{\frac{1}{2}} \\
 &= ([\text{Al}(\text{OH})_2^+]_D/[\text{Al}(\text{OH})_2^+]_S) \quad (8)
 \end{aligned}$$

To calculate the concentrations of the different species in the three compartments, the equations given above were combined with mass-balance relationships for Al, Ca, Na and HS (cf. Tipping *et al.*, 1988a). Iterative procedures were required because of the appearance of  $Z$  in both charge balance and exponential terms (e.g. Eqn. 3). For long-term predictive modelling of soil-rain interactions, where large numbers of sequential calculations are required, the CO5NBF routine from the Numerical Algorithms Group Library was used (Numerical Algorithms Group, 1983).

### CHOICE OF PARAMETER VALUES

Values of the fixed CHAOS parameters employed in this study are given in Table 2. Except where indicated, values estimated by Tipping *et al.*, (1988a) for humic acid isolated from the sediment of Mosedale Beck (a stream in Cumbria, UK) were used. Values of  $Ac$  and, in proportion,  $n$ , were changed to rescale the model in fitting data from soil experiments (see below). As will be seen, the chosen values provide reasonable descriptions of the soil data. Given more data all the parameters could be optimized, presumably improving the fit, but for present purposes the values given in Table 2 are adequate.

The most problematic parameter for assignment of values is  $V_D$ , the fractional diffuse layer volume. The values chosen are crude approximations based on notional humic specific surface areas of  $\sim 500 \text{ m}^2 \text{ g}^{-1}$ , combined with the Debye-Hückel parameter (Shaw, 1970). Calculations showed

**Table 2.** Values of parameters used in CHAOS

Parameter	Value
$Ac$ , total humic acidity, $\text{eq g}^{-1}$	$4.78 \times 10^{-3}$ , $3.01 \times 10^{-3}$ *
$n$ , content of COOH groups, $\text{eq g}^{-1}$	$2.51 \times 10^{-3}$ , $1.58 \times 10^{-3}$ *
Intrinsic equilibrium constants (Table 1 & Eqns 4, 5)	
$K_I$	$2.11 \times 10^{-3}$
$K_{II}$	$3.42 \times 10^{-5}$
$K_{Al}$	$1.65 \times 10^{-4}$
$K_{Al, H}$	$1.54 \times 10^{-5}$ , $2.37 \times 10^{-5}$ **
$K_{Ca}$	$1.63 \times 10^{-7}$
Constants in Eqn. 6.	
$P$	-1680
$Q$	-870
$V_D$ , fractional volume of diffuse layer	0.001; [HS] $\approx 2.5 \text{ g l}^{-1}$ , $I = 0.05 \text{ mol l}^{-1}$ 0.01; [HS] $\approx 2.5 \text{ g l}^{-1}$ , $I = 0.003 \text{ mol l}^{-1}$ 0.5; [HS] = $70 \text{ g l}^{-1}$ , $I = 0.0003 \text{ mol l}^{-1}$

\*The first value in each pair is for isolated Mosedale Beck humic acid, the second is estimated for soils in the present work (see text).

\*\*First value is for  $10^\circ\text{C}$ , second for  $16^\circ\text{C}$ . Other equilibrium constants are assumed to be temperature-independent (Tipping *et al.*, 1988a).

however, that rather large tolerances can be placed on  $V_D$ : for the cases shown in Table 2 referring to  $(\text{HS}) \approx 2.5 \text{ g l}^{-1}$ ,  $V_D$  could be halved or doubled without markedly affecting cation distributions. For  $[\text{HS}] = 70 \text{ g l}^{-1}$ , values of  $V_D$  in the range 0.3–0.7 gave reasonably similar results; calculated cation concentrations varied by less than a factor of 2, except  $[\text{Al}^{3+}]$  in compartment  $D$  which varied by up to a factor of 3. It should be noted that at  $[\text{HS}] = 70 \text{ g l}^{-1}$ , the estimated typical field value (see below), overlapping of diffuse layers is likely, so that the assignment of  $V_D$  becomes more uncertain. The major influence of  $V_D$  is in determining the proportions of charge-neutralizing cations in the diffuse layer; lowering  $V_D$  increases the concentrations of the more highly-charged ions at the expense of those of ions of lower charge and *vice versa*.

Equilibrium constants and enthalpy values of hydrolysis reactions of Al were as listed by Tipping *et al.* (1988b). Activity coefficients were calculated with the extended Debye-Hückel equation.

## EXPERIMENTAL

Mosedale is a glaciated valley in Cumbria, UK (Nat. grid SD 240030), with a flushed bog in its central part. The vegetation consists largely of *Nardus* grass, *Pteridium* bracken and *Sphagnum* moss. The underlying rocks are of the Borrowdale Volcanic Series. Four soil samples ( $A$ – $D$ ) were taken from the edges of the bog, a fifth ( $E$ ) from the waterlogged part. Material from the top 10 cm of the soil was taken. The samples were dark brown or black.

Water contents of unsieved soil were determined by loss in weight on drying at  $100^\circ\text{C}$ . The remainder of the work was done on material that had been passed, wet, through a 2 mm sieve. Organic contents were estimated by loss on ignition at  $550^\circ\text{C}$ . Contents of humic substances were estimated by extraction with NaOH as follows. Soil was suspended at a concentration of ca. 1 g (dry weight equivalent)  $\text{l}^{-1}$  in 0.01 M NaOH, the suspension was mixed end-over-end for 24 h, centrifuged and the supernatant solution analysed for dissolved organic carbon using a Phase Separations Tocsin II instrument. The solid residue was re-suspended in 0.01 M NaOH and the procedure repeated, the second extraction yielding 10% extra dissolved organic carbon. Estimates of the total amount of Al in compartments  $H$ ,  $D$  and  $S$  were made by extracting for 24 h with 0.01 M  $\text{HNO}_3$ /0.1 M  $\text{NaNO}_3$ , followed by analysis of the solution phase with pyrocatechol violet (Dougan & Wilson, 1974). Soil pH was determined on the solution phase obtained after adding 50  $\text{cm}^3$  of  $10^{-3}$  M NaCl to 50 g of soil and equilibrating for 24 h.

Batch titration experiments on the soils (which had been neither washed nor allowed to dry out) were performed as follows. Aqueous suspensions of concentration 6–11 g dry weight (equivalent)  $\text{l}^{-1}$  were prepared and 9  $\text{cm}^3$  aliquots placed in polycarbonate centrifuge tubes of 12  $\text{cm}^3$  capacity. Known amounts of acid ( $\text{HNO}_3$ ) or base (NaOH) and of neutral salt ( $\text{NaNO}_3$ ) were added to each tube and the suspension volumes made up to 10  $\text{cm}^3$ . The suspensions were allowed to equilibrate by end-over-end mixing for 24 h at  $16 \pm 2^\circ\text{C}$ , after which the solid and solution phases were separated by centrifugation and the supernatant analysed for pH, monomeric Al and absorbances at 340 and 600 nm.

Measurements of pH were made using a Radiometer PHM82 pH meter and GK2401C combination electrode, calibrated with buffers of pH 4.00 and 6.90, and with solutions of  $\text{HNO}_3$  of known concentration and ionic strength (pH 3–4.5). Monomeric aluminium in solution ( $\text{Al}_m$ ) was determined as described by Seip *et al.* (1984). Absorbance values at 340 nm (used to estimate HS in solution) were corrected for turbidity by making measurements at both 340 and 600 nm. The following equations hold:

$$A_{340}(\text{obs}) = A_{340}(\text{HS}) + A_{340}(\text{turbidity}) \quad (9)$$

$$A_{600}(\text{obs}) = A_{600}(\text{HS}) + A_{600}(\text{turbidity}) \quad (10)$$

from which we obtain

$$A_{340}(\text{HS}) = \frac{A_{340}(\text{obs}) - \beta A_{600}(\text{obs})}{1 - (\beta/a)} \quad (11)$$

where  $a = A_{340}(\text{HS})/A_{600}(\text{HS})$  and  $\beta = A_{340}(\text{turbidity})/A_{600}(\text{turbidity})$ . A value of  $a$  was obtained from measurements on filtered coloured supernatants,  $\beta$  was estimated from measurements on uncoloured turbid supernatants. Values of  $A_{340}(\text{turbidity})$  varied from 0–0.3 (1 cm cell), those of  $A_{340}(\text{HS})$  from 0 to 1.2. Humic concentrations were estimated from  $A_{340}(\text{HS})$  using an extinction coefficient of  $15 \text{ l g}^{-1} \text{ cm}^{-1}$ , determined for isolated Mosedale Beck humic acid.

The chemical speciations of  $\text{Al}_m$  in the supernatants were estimated assuming the only significant species present to be  $\text{Al}^{3+}$ , its monomeric hydrolysis products and organic complexes. Distributions among these forms were calculated as described by Tipping *et al.* (1988a) using organic complexation model III. Parameter values for isolated Mosedale Beck humic acid were employed for preliminary calculations. Speciations were refined after rescaling of  $A_c$  (cf. Table 2) as described below.

## RESULTS

Analytical information on the soil samples is given in Table 3. Each is high in organic matter, and approximately one-quarter of the dry weight consists of NaOH-extractable HS. The Al contents are assumed to represent metal complexed by the HS, present in the diffuse double layer, and in the bulk soil solution, but not to include Al in aluminosilicate mineral phases. The Al contents are similar to values published for organic soils by Cronan *et al.* (1986), determined by extraction with  $\text{CuCl}_2$ . In attempting to model solid-solution interactions, organic matter not extractable by NaOH is assumed inert, and all the Al extractable with 0.01 M  $\text{HNO}_3$ /0.1 M  $\text{NaNO}_3$  is assumed to be monomeric.

Table 3. Analytical data on soil samples

Sample	pH*	Analyses on dry weight basis			
		Water (%)	Organic matter (%)	Humic substances** (%)	Aluminium ( $\mu\text{mol g}^{-1}$ )
A	3.7	77	80	23	119
B	4.0	72	61	28	154
C	3.7	86	87	29	54
D	4.0	78	72	19	105
E	3.3	80	85	24	20

\*After adding  $50 \text{ cm}^3 10^{-3} \text{ M NaCl}$  to 50 g wet soil.

\*\*Calculated from NaOH-extractable organic carbon by assuming HS to be 50% C.

The results of batch titration experiments with the soil samples are presented in Figs 2 & 3. Concentrations of inorganic monomeric Al,  $[\text{Al}_m\text{-inorg}]$ , in the supernatant solutions were calculated from total, i.e. inorganic + organic monomeric, concentrations as described above. Data for  $\text{pH} \geq 5$  were ignored in order to be able to neglect carbonate equilibria: this meant the rejection of seven of the 90 data points obtained. Further data points were rejected if a substantial proportion ( $> 20\%$ ) of the monomeric Al in solution was calculated to be present as organically-complexed Al. This was a precaution against errors in the calculated concentrations of organically-complexed  $\text{Al}_m$  causing corresponding errors in the calculated concentrations of inorganic  $\text{Al}_m$ , and thence in the calculated activity of aluminium,  $\{\text{Al}^{3+}\}$ . Such errors would be more serious the greater the proportion of  $\text{Al}_m$  present as organic complexes.

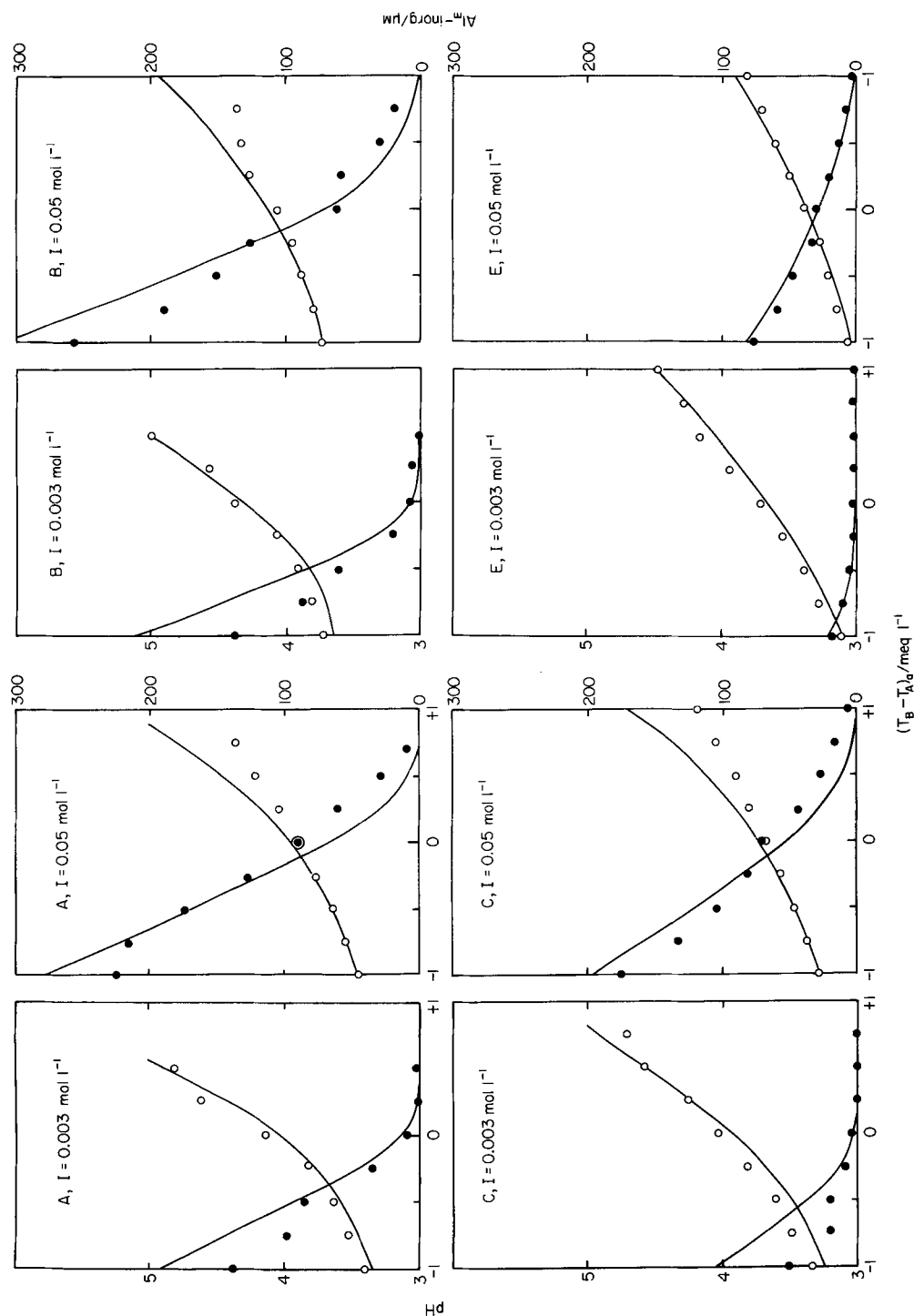


Fig. 2. Results of batch titration experiments with soil samples. Supernatant solution pH ( $\circ$ ) and concentration of monomeric inorganic Al ( $\bullet$ ) are plotted against added (base-acid). Soil concentrations (g dry weight equivalent  $\text{l}^{-1}$ ) were A 5.8, B 9.8, C 7.8, E 11.3. Points are experimental values, lines are predictions by CHAOS on the basis of total Al and HS concentrations.



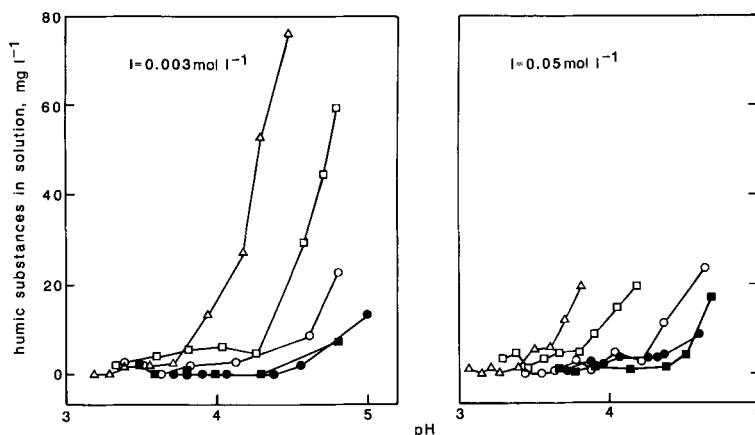


Fig. 3. Concentrations of HS in supernatant solutions plotted against pH for soils A (○), B (●), C (□), D (■) and E (△), at two ionic strengths.

In order to apply CHAOS to the remaining data (65 points), the parameter  $Ac$  was adjusted. Values of  $\{Al^{3+}\}$  and pH were used to calculate ionic distributions and for each data point the value of  $Ac$  was found for which the total calculated Al was equal to the analytically-determined value (cf. Table 3). While adjusting  $Ac$ , the proportion of humic carboxyl groups was kept constant, i.e. the parameter  $n$  was also adjusted so that the ratio  $n/Ac$  remained the same as in the isolated HS. In effect, this means that we found the concentration of 'active HS' in the soil samples. The results of the calculations are summarized in Table 4. It is seen from the tolerably small standard deviations that the calculated individual values of  $Ac$  are reasonably constant for a given soil, and further that  $Ac$  varied little among soils. The overall mean value of  $Ac$  is 0.63 times that estimated for isolated Mosedale Beck humic acid. Possible reasons for the difference are (a) that the soil HS have fewer functional groups per gram than the stream bed material, (b) that the soil suspensions contain a competitor (with  $H^+$  and  $Al^{3+}$ ) for humic binding sites, e.g. iron, (c) that the HS in the soil are incompletely solvated so that not all the humic functional groups are available for complexation, (d) that there is in fact no difference in  $Ac$  values, but other model parameters require adjustment. In any event we consider that decreasing  $Ac$  to 0.63 times the 'starting value' is a relatively minor adjustment. The values of  $n$  obtained correspond to approximately 40 meq  $g^{-1}$  soil, of similar magnitude to acidity values of organic soils estimated by titration to an arbitrary neutral pH value (Bache 1984).

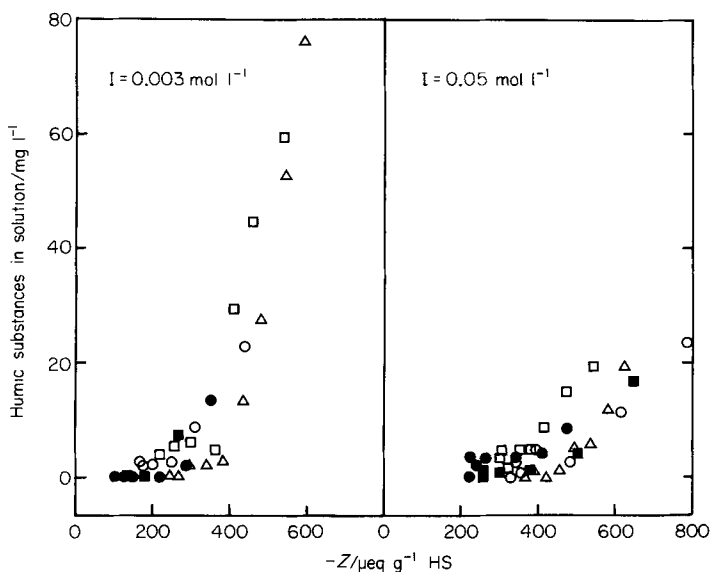
Having obtained a mean  $Ac$  for each soil, the dependence of  $[Al_m\text{-inorg}]$  and pH on the concentrations of added acid or base could be calculated, although this requires an estimate of the concentration of mineral acid or base present before any additions were made. We can write

$$(T_B - T_A) = (T_B - T_A)_o + (T_B - T_A)_a \quad (12)$$

where  $(T_B - T_A)$  is the actual difference in total base and acid concentrations,  $(T_B - T_A)_o$  is the difference before any additions, and  $(T_B - T_A)_a$  is the difference in added base and acid. First it was assumed that  $(T_B - T_A)_o$  was zero, then  $[Al_m\text{-inorg}]$  and pH were calculated from  $T_{Al}$ ,  $T_{HS}$  (total concentrations of Al and HS, respectively) and  $(T_B - T_A)_a$ . Next, plots of  $[Al_m\text{-inorg}]$  and pH against  $(T_B - T_A)_a$  were constructed and compared with the experimental points. The value of  $(T_B - T_A)_o$  was taken to be the average difference between points of the same  $[Al_m\text{-inorg}]$  or pH (see Table 4). This enabled the calculated plots and experimentally-determined points to be matched (Fig. 2). It is seen that the model reproduces reasonably well the experimental results, bearing in mind that only one parameter ( $Ac$ ) has been adjusted. With more extensive data for soils, comprehensive parameter optimization could be carried out, presumably resulting in improved fits. However, the present analysis demonstrates that CHAOS is a useful model for organic soils.

**Table 4.** Calculated values of  $Ac$  (mean and SD) and of  $(T_B - T_A)_o$  (see text)

Soil	No. of data points	Mean $Ac$ (meq g <sup>-1</sup> )	$(T_B - T_A)_o$ (μmol l <sup>-1</sup> )
A	12	3.57 (0.34)	-20
B	14	2.98 (0.22)	+150
C	12	2.31 (0.28)	+130
D	13	3.01 (0.15)	-30
E	14	3.15 (0.45)	+210
all	65	3.01 (0.50)	—

**Fig. 4.** Data in Fig. 3 plotted against calculated values of  $Z$ , the net humic charge. Symbols as for Fig. 3.

The experiments with the soil samples provide an opportunity to consider the solubilization of HS in terms of net humic charge,  $Z$ . It is well known that the fewer protons or metal ions are bound by HS, the greater is their solubility (Hayes & Swift, 1978). This is illustrated by the plots in Fig. 3 which show increasing amounts of HS in solution as the pH increases, the effect being more marked the lower the  $Al/HS$  ratio (see Table 3). The results for the five soils can be made more-or-less coincident by plotting  $[HS]$  in solution against  $Z$  calculated using CHAOS (Fig. 4), indicating that concentrations of HS in soil solution could be quantitatively predicted on the basis of extents of complexation by protons and metal ions. This finding bears out work with aquatic HS (Tipping *et al.*, 1988a).

### PREDICTIVE CALCULATIONS

In this section we consider the use of CHAOS to predict the compositions of solutions in contact with organic soils. Ionic distributions are calculated for a hypothetical soil subjected to inputs of

rain of different composition, and the times taken to change from one set of conditions to another are examined. The calculation procedure involves the stepwise replacement of the solution in compartment *S* by fresh input solution ('rain'), and the computation of the equilibrium distributions of ions at each step. For ease of exposition, it is arranged that steady states can be achieved, by supplying Al at rates sufficient to keep the total Al concentration,  $T_{\text{Al}}$ , constant.

First let us consider an organic soil with a bulk composition representative of those taken from Mosedale (Table 3), with inputs of a simplified 'acid rain' (see Table 5 for composition). The calculated steady state concentrations of species involved are shown in Tables 5 & 6, column 1. The composition of compartment *S* is seen to be similar to that of the rain, with a small replacement of  $\text{H}^+$  by  $\text{Al}^{3+}$  and  $\text{AlOH}^{2+}$ . The Al is largely in compartment *H*, i.e. complexed by the HS, whereas the

**Table 5.** Steady-state ionic distributions. The rain input to soil in columns 1 and 3 had the composition  $\text{Ca}^{2+}$ , 50  $\mu\text{M}$ ;  $\text{Na}^+$ , 100  $\mu\text{M}$ ;  $\text{H}^+$ , 50  $\mu\text{M}$ ;  $\text{X}^-$ , 250  $\mu\text{M}$ ; that to soil in columns 2 and 4 had the composition  $\text{Ca}^{2+}$ , 50  $\mu\text{M}$ ;  $\text{Na}^+$ , 100  $\mu\text{M}$ ;  $\text{H}^+$ , 10  $\mu\text{M}$  and  $\text{X}^-$ , 210  $\mu\text{M}$ . For soil in columns 3 and 4, 25  $\mu\text{M}$   $\text{Ca}^{2+}$  from rain was assumed to be taken up by plants in exchange for 50  $\mu\text{M}$   $\text{H}^+$ . 'Compensating cations' are those in compartment *D*; the percentages refer to the contribution of each cation to countering the charge on the humic substances

Component	Column			
	1	2	3	4
<i>Soil</i>				
$T_{\text{HS}}$ ( $\text{g l}^{-1}$ )	70	70	70	70
$T_{\text{Al}}$	25 000	25 000	25 000	25 000
$T_{\text{Ca}}$	6520	14400	2250	4110
$T_{\text{Na}}$	850	1150	715	950
<i>Compartment H</i>				
Al	336	355	309	318
Ca	2	33	0.3	0.8
<i>Compartment D</i>				
$\text{Al}^{3+}$	3000	235	6700	5430
$\text{AlOH}^{2+}$	13	4	18	18
$\text{Ca}^{2+}$	12 700	24 200	4420	8100
$\text{Na}^+$	1590	2200	1330	1800
$\text{H}^+$	760	220	1210	1030
<i>Compartment S</i>				
$\text{Al}^{3+}$	0.74	0.02	2.85	0.93
$\text{AlOH}^{2+}$	0.05	0.01	0.10	0.05
$\text{Ca}^{2+}$	50	50	25	25
$\text{Na}^+$	100	100	100	100
$\text{H}^+$	47.7	10	91.2	57.1
pH	4.33	5.01	4.05	4.25
Net humic charge ( $\mu\text{eq g}^{-1}$ )	-263	-368.0	-225.0	-253
<i>Compensating cations (%)</i>				
$\text{Al}^{3+}$	24	1	64	46
$\text{AlOH}^{2+}$	0	0	0	0
$\text{Ca}^{2+}$	69	94	28	46
$\text{Na}^+$	4	4	4	5
$\text{H}^+$	2	0	4	3

Ca and Na are largely in the diffuse part of the electrical double layer, compartment *D*. The charge on the HS is  $-263 \mu\text{eq g}^{-1}$ , probably too low for much humic material to go into solution. Compensation of the humic charge is mainly by  $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$  (in compartment *D*).

The concentration of  $\text{Al}^{3+}$  in the soil solution is calculated to be approximately  $1 \mu\text{M}$ . This is in reasonable agreement with field observations. For example, Nilsson & Bergkvist (1983) reported mean values of  $[\text{Al}^{3+}]$  of 0.3 to  $8 \mu\text{M}$  for soil waters of pH 3.76–4.24, Driscoll *et al.* (1985) found  $[\text{Al}^{3+}] \approx 0.2$  to  $5 \mu\text{M}$  for a pH range of 3.62–4.95, Cronan *et al.* (1986) found  $[\text{Al}^{3+}] \approx 0.1$  to  $10 \mu\text{M}$  for pH 3.6–4.0. As pointed out by the last-named authors, these concentrations are considerably lower than would be expected for equilibrium with an aluminium hydroxide phase, for which  $[\text{Al}^{3+}] \sim 100 \mu\text{M}$  might be found at pH 4.3. As with the Al/humic adsorption model of Cronan *et al.* (1986), CHAOS explains the undersaturation by interactions with soil HS. When high concentrations of Al are found in organic soil solutions this is due to organically-complexed Al (David & Driscoll, 1984).

Now let us consider the effect of reducing the rain acidity by 80%, to give a rain pH of 5.01. For the same soil the ionic distributions are given in Tables 5 & 6, column 2. As expected, the pH of the soil solution is very similar to that of the rain, the Al concentration in compartment *S* now being very small. The humic charge, now compensated for almost entirely by  $\text{Ca}^{2+}$ , is considerably increased compared to the 'acid rain' steady state, and is probably sufficiently great for HS to pass into solution. Thus, one consequence of reducing rain acidity might be to raise the concentration of dissolved organic matter in soil water. There is palaeolimnological evidence that the reverse process, i.e. diminution of dissolved organic matter concentrations, accompanied acidification (Davis *et al.*, 1985).

**Table 6.** Cation distributions and base saturations for the steady-states of Table 5. To calculate cation equivalents per g of soil, it was assumed that HS comprise 25% of the soil dry weight (cf. Table 3). The apparent base saturation was calculated by assuming that the conventionally-estimated cation exchange capacity would be equivalent to  $n$ , i.e.  $1.58 \text{ meq g}^{-1}$  HS or  $0.395 \text{ meq g}^{-1}$  soil, and dividing this into the sum of the equivalents of  $\text{Ca}^{2+}$  and  $\text{Na}^{+}$  in compartment *D*. The 'base saturation in terms of  $Z$ ' was calculated by considering the contributions of  $\text{Ca}^{2+}$  and  $\text{Na}^{+}$  in compartment *D* to the balancing of charge in compartment *H*

Constituent	Compartment	Composition ( $\mu\text{eq g}^{-1}$ soil) column			
		1	2	3	4
Al	<i>H</i>	252.0	267.0	232.0	239.0
	<i>D</i>	16.0	1.0	36.0	29.0
	<i>S</i>	0.0	0.0	0.0	0.0
	total	268.0	268.0	268.0	268.0
Ca	<i>H</i>	1.0	16.5	0.2	0.4
	<i>D</i>	45.3	86.4	15.8	28.9
	<i>S</i>	0.2	0.2	0.1	0.1
	total	46.5	103.1	16.1	29.4
Na	<i>H</i>	0.0	0.0	0.0	0.0
	<i>D</i>	2.8	3.9	2.4	3.2
	<i>S</i>	0.2	0.2	0.2	0.2
	total	3.0	4.1	2.6	3.4
Apparent base saturation (%)		12.0	23.0	5.0	8.0
Base saturation in terms of $Z$ (%)		73.0	98.0	32.0	51.0

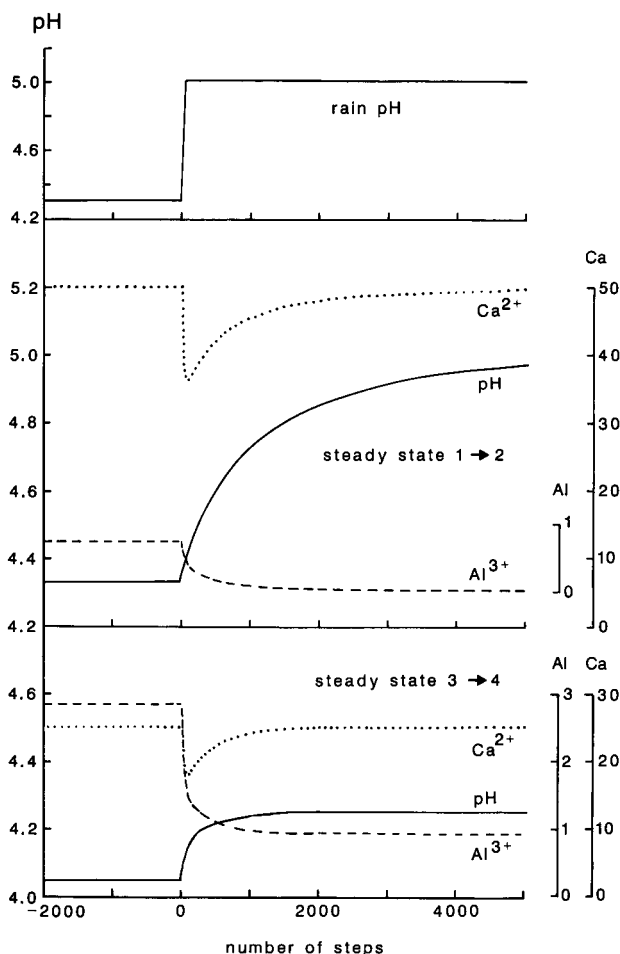


Fig. 5. Predictions of soil solution composition (compartment  $S$ ) during conversion between steady states (see Table 5). Steady-states 1 and 3 are for soils subjected to 'acid rain' of pH 4.31, 2 and 4 are for the same soils subjected to 'rain' of pH 5.01. For a 10 cm depth of soil and rainfall of 2 m  $a^{-1}$ , 1000 steps represent ca. 20 years. Concentrations of Al and Ca are  $\mu M$ .

In columns 3 and 4 of Tables 5 & 6, ionic distributions are given for situations in which acid is imparted to the soil by the exchange of rain  $Ca^{2+}$  for  $H^+$ , as a result of plant growth (cf. van Breemen *et al.*, 1984). Comparison with the values in columns 1 and 2 shows that the additional acid input causes decreases in pH and increases in  $[Al^{3+}]$  in the soil water, lowers the humic charge, and lessens the effect of reducing rain acidity.

Now let us consider how long it takes for one steady-state to change to another. Calculations for conversions between the steady-states referred to in Tables 5 and 6, are presented in Fig. 5. In each case the change in rain composition is assumed to take place over 50 steps (typically equivalent to 1 year—see below). The plots in Fig. 5 show that changes in soil solution composition lag considerably behind the change in the rain, and that the conversion from steady-state 3 to steady-state 4 requires fewer steps than that from 1 to 2. Although the steady-state concentrations of  $Ca^{2+}$  in compartment  $S$ — $[Ca^{2+}]_S$ —are the same for 'acid' and 'less-acid' rain, sharp decreases in  $[Ca^{2+}]_S$  are predicted to occur immediately following the change in rain composition. These decreases are the immediate response to the lower value of  $[X^-]_S$ , which is ultimately compensated for by lower  $[H^+]_S$  and  $[Al^{3+}]_S$ .

How do the steps in the calculations relate to real time? For a soil with a volume of replaceable water of  $w \text{ m}^3 \text{ per m}^2$ , subjected to rainfall of  $r \text{ m a}^{-1}$  the residence time of the water, assuming all of it to infiltrate, and with no evapotranspiration, is  $w/r \text{ a}$ . For a soil depth of 10 cm, and a soil water content of 80% by volume of which half is replaceable,  $w = 0.04 \text{ m}$ . The residence time for  $r = 2 \text{ m a}^{-1}$  is, therefore, 0.02 a, so that 50 calculation steps represent 1 year of rain-soil interaction. Referring to Fig. 5 we see that to pass from one steady-state to another would take tens to hundreds of years for these conditions. Conversions in the opposite direction (less acid  $\rightarrow$  acid;  $2 \rightarrow 1$ ,  $4 \rightarrow 3$ ) are calculated to require similar time periods. The changes would be proportionately quicker for thinner soils, slower for deeper ones.

## CONCLUSIONS

The finding that CHAOS accounts quite well for the results of the laboratory experiments encourages the belief that mechanistically-based, quantitative descriptions of ion-binding in organic soils are possible, and that humic solubility may also be predictable. There is, of course, scope for development and improvement. Probably the most simplified features of the model are first the use of the Donnan equilibrium, combined with the semi-arbitrary assignment of values of  $V_D$ , to describe distributions of ions between the diffuse double layer and the bulk solution, and second the restricted formulation of the abundances and types of ion-binding sites. More realistic descriptions of these could certainly be obtained, although not without introducing more parameters. Further testing of the model on more soil samples and on isolated humic substances is required to find out if such improvements are needed. It may also be desirable to fit experimental data by optimizing all the parameters, rather than simply adjusting the contents of humic functional groups ( $Ac$  and  $n$  in proportion) as done in the present work.

Calculations with CHAOS (Tables 5 & 6, Fig. 5) suggest that, although acidified organic soils will respond to reductions in depositional acidity, the full response may require quite long time-periods. However, signs of 'improvement' (noticeable decreases in  $[\text{Ca}^{2+}]_S$ ,  $[\text{Al}^{3+}]_S$  and  $[\text{H}^+]_S$ ) could be expected on shorter time-scales. It is also predicted that soils are rather finely-poised with regard to concentrations of HS in solution, and that concentrations might increase following a reduction in rainfall acidity. This could have important consequences for leaching processes in lower soil horizons and, where organic soils are present in reservoir catchments, for water treatment.

With regard to the last point, a final comment is appropriate. It is sometimes suggested that the dissolution of organic acids acidifies water. If, referring to Fig. 1, we regard the dissolution process as the transfer of a part of compartments  $H + D$  (i.e. a humic molecule and its diffuse double layer) to compartment  $S$ , it is clear that this will not affect the ionic composition of the rest of compartment  $S$ , except for minor changes due to alterations in humic solvation and/or conformation. The main acidifying effect of HS is not their dissolution; it is their formation and dissociation. The importance of humic dissolution is in the behaviour of the soil solution when its equilibrium is disturbed. For example, humic-rich solutions are better-buffered against additions of acid or base.

## ACKNOWLEDGEMENTS

We thank M. Hornung (Institute of Terrestrial Ecology, Bangor) and D. G. Kinniburgh (British Geological Survey, Wallingford) for their constructive comments on a draft manuscript. We are grateful to B. James, M. Ohnstad and C. Woof for technical support, and to H. Gardberg for typing the draft and final versions of the manuscript. Financial support came from the Commission of European Communities, the Natural Environment Research Council and the Royal Society Surface Waters Acidification Programme.

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(Received 14 May 1987)